



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US99/19242 <b>(22) International Filing Date:</b> 23 August 1999 (23.08.99)  <b>(30) Priority Data:</b> 09/138,510                      24 August 1998 (24.08.98)                      US  <b>(71) Applicant:</b> THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US).  <b>(72) Inventors:</b> STOKICH, Theodore, M., Jr.; 4119 Cruz Drive, Midland, MI 48642 (US). MARTIN, Brian, B.; 5608 Onna Lane, Midland, MI 48640 (US). STRANDJORD, Andrew, J.; 85 Ajo Way, Colorado Springs, CO 80132 (US). HETZNER, Jack, E.; 5586 Holland Road, Saginaw, MI 48601 (US). HARRIS, Robert, F.; 1213 East Redbud Street, Celina, TX 75009 (US). TOWNSEND, Paul, H., III; 1102 Willard Street, Midland, MI 48642 (US). FRYE, Donald, C.; 411 Rollcrest Court, Midland, MI 48640 (US). SCHMIDT, Donald, L.; 2412 Saint Marys Drive, Midland, MI 48640 (US).  <b>(74) Agent:</b> ZERULL, Susan, Moeller, The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		<b>(81) Designated States:</b> CN, JP, KR, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> ADHESION PROMOTER AND SELF-PRIMING RESIN COMPOSITIONS AND ARTICLES MADE THEREFROM  <b>(57) Abstract</b>  A composition is comprised of the following: a) a hydrolyzed or partially hydrolyzed silane selected from alkoxysilanes and acyloxysilanes; b) a solvent consisting of an organic liquid or mixture of two or more organic liquids in which component (a) and component (c) are soluble and c) a cross-linking prepolymer, oligomer, resin or mixtures thereof that forms a low dielectric constant cross-linked polyarylene. A coating may be made using the composition wherein the coating is comprised of a cross-linked polymer of a low dielectric cross-linking prepolymer, oligomer, resin or mixture thereof and a hydrolyzed or partially hydrolyzed silane, said coating being adhered to a surface of a substrate wherein said surface is comprised of a first material that is a metal, ceramic or polymer and a second material that is (i) a metal, ceramic, or polymer and (ii) different than the first material.		

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## ADHESION PROMOTER AND SELF-PRIMING RESIN COMPOSITIONS AND ARTICLES MADE THEREFROM

The present invention relates to a coating composition and more particularly to a solution of a hydrolyzed or partially hydrolyzed alkoxysilane, and a cross-linking polymeric resin (e.g., polyarylene and polyphenylene resin) that produces a low dielectric constant polymer.

Hydrolyzed alkoxysilanes have been used as adhesion promoters or coupling agents for arylcyclobutene resins. However, these alkoxysilanes generally have not successfully coated substrates having surfaces composed of more than one material (e.g., silicon, silicon dioxide, silicon nitride, various metals, and other materials found in a microelectronic device).

The hydrolyzed alkoxysilanes are typically used as a primer layer, i.e., they are applied to the substrate first, followed by application of the polymeric material. The alkoxysilanes are typically hydrolyzed to form aqueous and/or protic solutions before being applied as thin films. However, many organoalkoxy-silanes are not soluble in water and must be dissolved first in a compatible organic solvent, such as an alcohol. Unfortunately, upon application of the aqueous alkoxysilane/alcohol mixture, a discontinuous film may form which contains voids where the film has not covered the substrate.

It is also known that a hydrolyzed alkoxy-silane can be used as an adhesion promoter primer layer for arylcyclobutene resins. For example, in Proc. MRS, Vol. 323, pg. 365, 1994, *Adhesion of Cyclotene™ (BCB) Coatings on Silicon Substrates*, a prehydrolyzed solution of 3-methacryl-oxypropyltrimethoxysilane (MOPS) in methanol was used as an adhesion promoter for CYCLOTENE™. However, the MOPS solution is extremely difficult to deposit uniformly, forming agglomerates on the surface, which leads to reliability problems when used in fabricated parts.

This is particularly evident when the substrate surface is comprised of more than one material such as a microelectronic device (e.g., integrated circuit, multichip module and flat panel display). A microelectronic device may be comprised of many materials that need to be adhered to by a coating. Materials at the surface of these devices may include, for example, silicon, aluminum, copper, tungsten, silver, gold, platinum, other polymers (e.g., epoxies, polyimides and polyamides), ceramics (e.g., silicas, titanium nitrides, silicon nitrides and silicon oxynitrides).

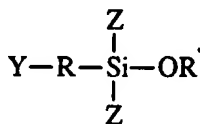
WO96/11990 taught that hydrolyzed or partially hydrolyzed alkoxysilanes may be added to a solution of arylcyclobutene to form a self-priming composition.

Polyarylene compositions, such as notably the polyphenylenes of WO 98/11149, are becoming increasingly the polymers of choice as thin film dielectrics in the electronics industry. Unfortunately, adhesion of these polymers is occasionally insufficient. Therefore, a polyarylene composition that has improved adhesion without sacrificing the dielectric properties, or coating properties is desired.

Another group of polyphenylenes are the poly(arylene ethers) (ie PAE\* resins – Air Products) are described in EP 0 755 957 B1 6/5/99 and/or the Flare\* resins made by Allied Signal Corp (see N.H. Hedricks and K.S.Y Liu, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chm.) 1996, 37(1), 150-1; also J.S. Drage et al., Material Res. Soc. Symp. Proc. (1997), Volume 476 (Low Dielectric Constant Materials III), 121-128.

One aspect of the present invention is a coating composition comprising:

- a) a silane selected from hydrolyzed or partially hydrolyzed alkoxysilane and hydrolyzed or partially hydrolyzed acyloxysilanes,
- b) a solvent consisting of an organic liquid or mixture of two or more organic liquids in which component (a) and component (c) are soluble and
- c) a cross linking prepolymer, oligomer, resin or mixtures thereof that forms a low dielectric constant crosslinked polyarylene. In a preferred embodiment, the silane is of the formula:



wherein R is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Y is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, or 3-amino; R' is independently in each occurrence C<sub>1</sub>-C<sub>6</sub> alkyl or acyl; and Z is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl or OR'.

The coating compositions of the present invention offer advantages such as a separate adhesion promoter application step is not required and a coating can be prepared that is uniformly adhered to a substrate where the substrate surface is comprised of more than one material such as an microelectronic device.

In another aspect, the present invention is an article comprising:

- (a) a substrate that has a surface having a first region of a first material comprising a metal, ceramic or polymer and a second region of a second material comprising (i) a metal, ceramic or polymer that is different than the first material and

(b) a coating adhered to the surface of the substrate, the coating being comprised of a crosslinked low dielectric polyarylene of a crosslinking prepolymer, oligomer, resin or mixtures thereof and a silane selected from hydrolyzed or partially hydrolyzed alkoxysilanes and hydrolyzed or partially hydrolyzed acyloxysilanes..

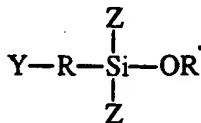
5 Adhered, herein, is when the coating has a bond strength to the substrate of at least about 80 MPa regardless of the material the coating is bonded. Preferably the bond strength is at least about 100 MPa, more preferably at least about 125 MPa and most preferably at least about 200 MPa. Alternatively, adhered is when the coating passes the tape peel test described by ASTM Test Method D3359(B). Generally, the coating fails to  
10 pass the tape peel test when any part of the coating has bond strength of less than about 80 MPa.

Different material herein means the first material has a different chemistry than the second material. For example, the materials may be two different metals (e.g., copper and aluminum), two different ceramics (silica and alumina), two different polymers (e.g.,  
15 polyimide and polyamide), a ceramic and a metal, a ceramic and a polymer, or a metal and a polymer.

The coating compositions of the present invention are useful in a variety of applications, including coatings for multichip modules, flat panel displays and integrated circuits.

20 The silanes may be any alkoxysilane, acyloxysilane or mixture thereof capable of forming a solution with the cross linking prepolymer, oligomer, resin or mixtures thereof (herein referred to as polymer precursors) in an organic liquid. Preferably, the alkoxysilanes are dialkoxy or trialkoxysilanes and the acyloxysilanes are diacyloxy or triacyloxysilane. More preferably, the silanes correspond to the formula (I):

25



wherein R is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, preferably of 6 to 20 carbon atoms, or a direct bond; Y is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, aryl (preferably of 6 to 20 carbon atoms), 3-  
30 methacryloxy, 3-acryloxy, 3-aminoethylamino, or 3-amino; R' is independently in each occurrence C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>1</sub>-C<sub>6</sub> acyl; and Z is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl or OR'.

The term alkylidene refers to aliphatic hydrocarbon radicals wherein attachment

occurs on the same carbon. The term alkylene refers to radicals which correspond to the formula  $-(C_nH_{2n})-$ . The term aryl refers to an aromatic radical, aromatic being defined as containing  $(4n+2)$  electrons as described in Morrison and Boyd, *Organic Chemistry*, 3rd Ed., 1973. The term arylene refers to an aryl radical having two points of attachment. The term alkyl refers to saturated aliphatic groups such as methyl, ethyl, etc. Alkenyl refers to alkyl groups containing at least one double bond, such as ethylene, butylene, etc. Acyl refers to a group having  $-C(O)R$  structure. Acyloxy refers to groups having  $-OC(O)R$  structure. The groups previously described may also contain other substituents, such as halogens, alkyl groups, aryl groups, and hetero groups such as ethers, oximino, esters, amides; or acidic or basic moieties, i.e., carboxylic, epoxy, amino, sulfonic, or mercapto, provided the alkoxysilane remains compatible with the other components of the coating composition.

Preferably the silane is a trialkoxy-silane such as 3-ethacryloxypropyltrialkoxysilane, 3-aminopropyltrialkoxysilane, 3-aminoethylaminopropyl-trialkoxysilane, a vinyltrialkoxysilane, a benzyltri-alkoxysilane, a bicycloheptenyltrialkoxysilane, a cyclohexenylethyltrialkoxysilane, a cyclohexyltri-alkoxysilane, a cyclopentadienylpropyltrialkoxysilane, a 7-octa-1-enyltrialkoxysilane, a phenethyltrialkoxysilane, an allyltrialkoxysilane or an acetoxysilane. The silane is even more preferably 3-methacryloxypropyl-trimethoxysilane, vinyltriacetoxysilane, vinyltrimethoxysilane and vinyltriethoxysilane. The silanes are preferably hydrolyzed or partially hydrolyzed by the solventless process described hereinafter and can be used directly in the coating compositions. However, some of the silanes hydrolyze so easily that hydrolysis prior to use in the composition of the present invention is not necessary. These silanes hydrolyze self-catalytically when used in the composition of the present invention such that upon application to a substrate, the silane is hydrolyzed by ambient air humidity. The silane may also be hydrolyzed by water present in the solvent, polymer precursors or mixtures thereof contained in the composition. Such silanes can be defined as silanes which, upon contact with water in the absence of a catalyst, hydrolyze in about 30 minutes or less. Examples of such silanes include 3-aminopropyltriethoxysilane and 3-aminoethylamino-propyltriethoxysilane. Alternatively, the hydrolyzed or partially hydrolyzed silane can be prepared in a volatile solvent. If desirable, all or most of the solvent may be removed prior to being incorporated into the coating composition of the present invention.

The silanes useful in the practice of the present invention can be made by techniques well known in the art such as exemplified in *Encyclopedia of Chemical Technology*, Third Edition, Volume 20, pp. 916-918, 1982 and *Silane Coupling Agents* by Edwin P. Plueddemann, Chapter 2, pp. 30-31, 1982.

The solvent used in the film forming coating composition of the present invention can be any organic liquid or mixture of two or more organic liquids in which the adhesion promoter and the polyarylene are soluble to produce a film forming composition. The solvent is preferably an aprotic solvent or one which is highly immiscible with water.

5 Representative examples of solvents include aromatic hydrocarbons, ketones, esters, ethers or mixtures thereof. Preferably, the solvent is an aromatic hydrocarbon, more preferably cyclohexanone, mesitylene, gammabutyrolactone, N-methylpyrrolidinone (NMP) or a mixture thereof.

10 The polymer precursor used in the film forming coating compositions may be any capable of forming a solution with the hydrolyzed silane in the organic liquid described previously and capable of forming a low dielectric constant crosslinked polymer after curing. A low dielectric constant crosslinked polymer is any that is an electrical insulator and has a dielectric constant of at most about 3, preferably at most about 2.5 and most preferably at most about 2.2. However, herein, the low dielectric constant crosslinked polymer does not  
15 include an epoxy, polyimide, polyamide, or arylcyclobutene. Crosslinked polymer, herein, is used as understood in the art and described by "cross-linking" in Hawley's Condensed Chemical Dictionary 12<sup>th</sup> Edition, Van Nostrand Reinhold Co., New York, NY, 1993.

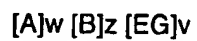
Desirably, the crosslinked polymer is hydrophobic. As an illustration, the crosslinked polymer preferably has a water absorption of at most about 0.5%, more preferably at most  
20 about 0.2% and most preferably at most about 0.1% by weight of the crosslinked polymer. The water absorption may be determined by known methods. Generally, the glass transition temperature is at least about 200°C and more preferably at least about 250°C. It is also desirable that the crosslinked polymer has excellent thermal stability. That is to say, the crosslinked polymer fails to decompose substantially at temperatures less than about  
25 450°C. For example, the crosslinked polymer desirably loses less than 1% of its weight when exposed to a temperature of 400°C for 24 hours.

Preferred crosslinked polymers polyarylenes including polyphenylenes as disclosed for example in WO98/11149 and polyarylene ethers. Suitable polyarylene ethers include those known in the art such as described in U.S. Patent Nos. 5,115,082; 5,155,175;  
30 5,179,188 and 5,874,516 and in PCT WO 91/09081; WO97/01593 and EP 0755957-81.

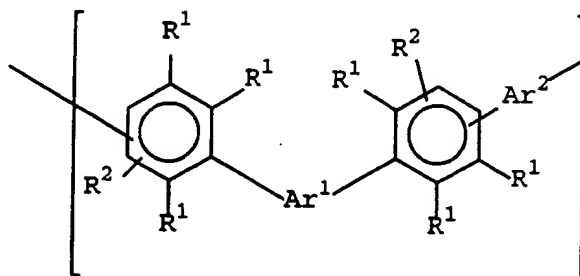
Any suitable polyphenylene may be used in the present invention such as those described by Wrasidlo and Augl, in J. Poly, Sci., Part B (1969) and U.S. Patent Nos. 5,334,668; 5,236,686; 5,169,929 and 5,338,823. Preferably the polyphenylene is one  
35 described in WO98/11149,. The oligomers and polymers and corresponding starting

monomers of the preferred polyphenylenes are as follows.

- I. Oligomers and polymers of the general formula:

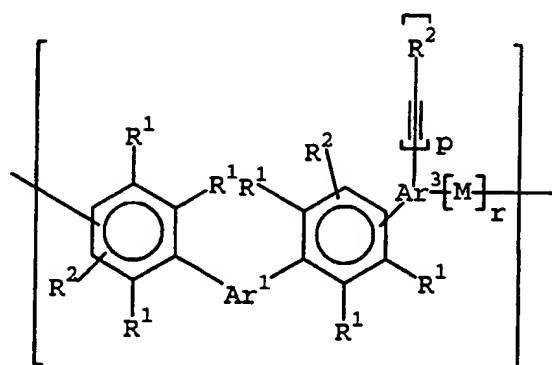


wherein A has the structure:



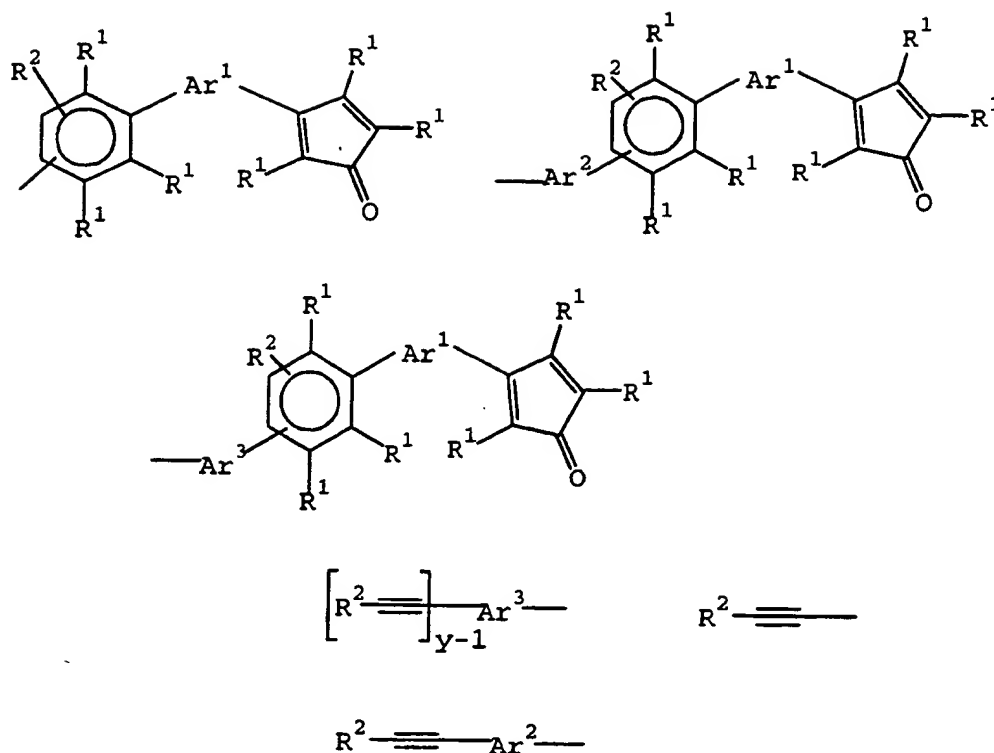
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and B has the structure:



wherein EG are end groups having one or more of the structures:

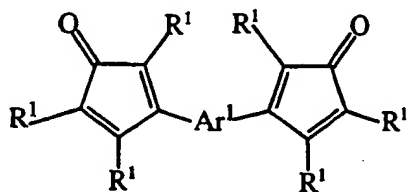




wherein R<sup>1</sup> and R<sup>2</sup> are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar<sup>1</sup>, Ar<sup>2</sup> and Ar<sup>3</sup> are independently an unsubstituted aromatic moiety or inertly-substituted aromatic moiety, M is a bond, and y is an integer of three or more, p is the  
 5 number of unreacted acetylene groups in the given mer unit, r is one less than the number of reacted acetylene groups in the given mer unit and p+r=y-1, z is an integer from 0 to about 1000; w is an integer from 0 to about 1000 and v is an integer of two or more.

Such oligomers and polymers can be prepared by reacting a  
 10 biscyclopentadienone, an aromatic acetylene containing three or more acetylene moieties and, optionally, a polyfunctional compound containing two aromatic acetylene moieties. Such a reaction may be represented by the reaction of compounds of the formulas:

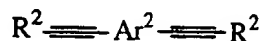
(a) a biscyclopentadienone of the formula:



(b) a polyfunctional acetylene of the formula:



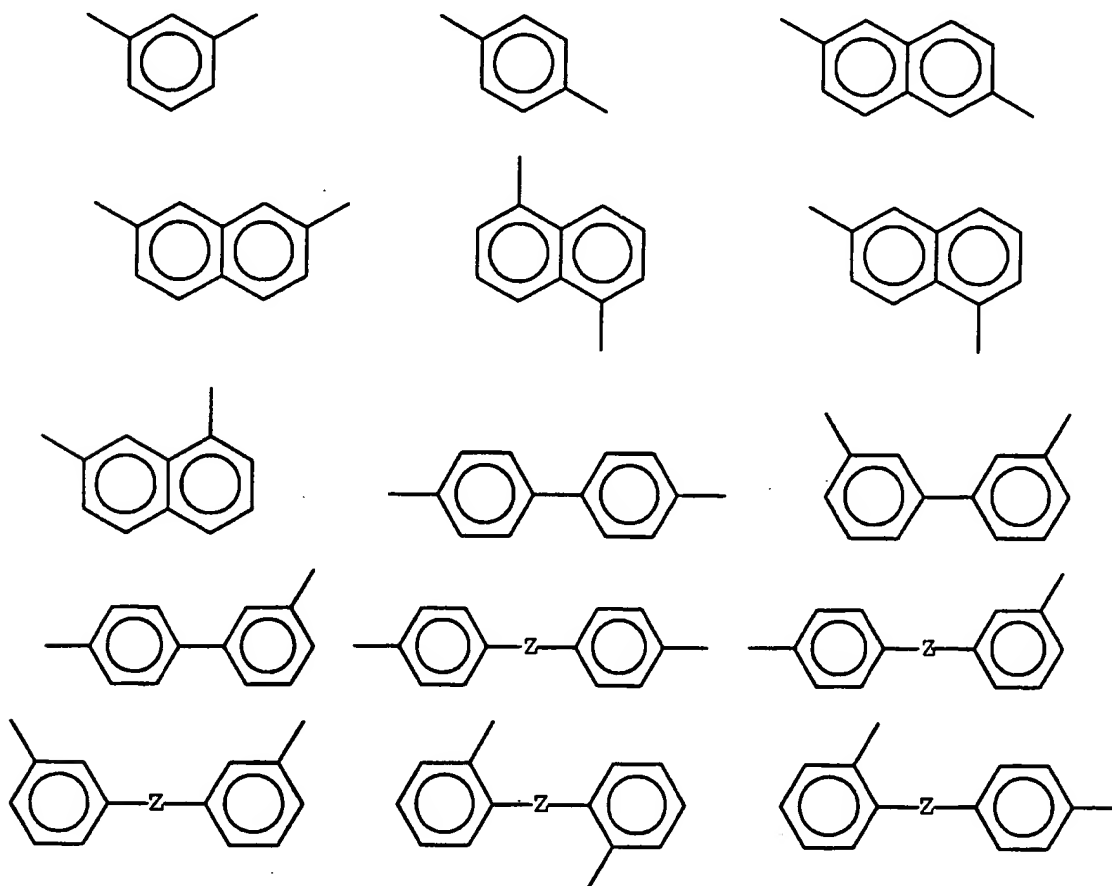
(c) and, optionally, a diacetylene of the formula:

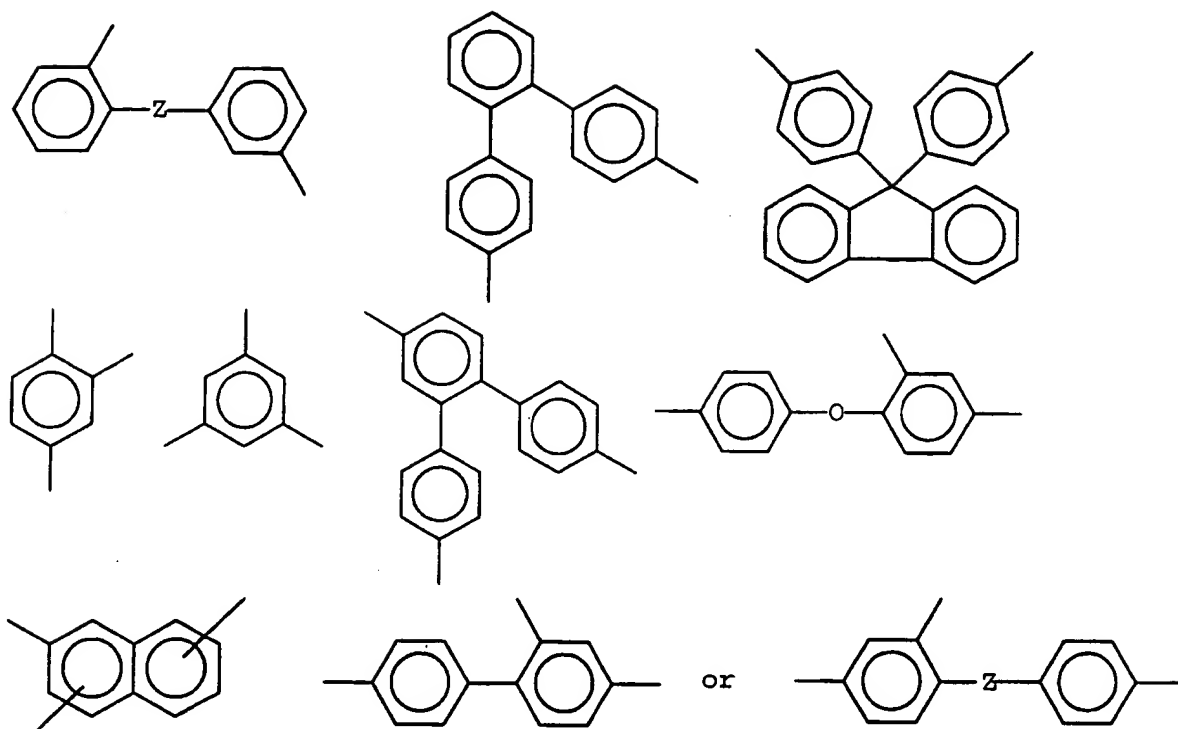


wherein  $R^1$ ,  $R^2$ ,  $Ar^1$ ,  $Ar^2$ ,  $Ar^3$  and  $y$  are as previously defined.

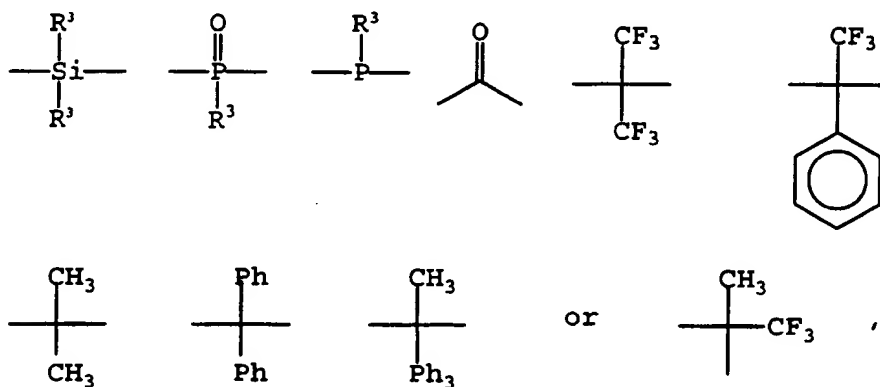
- 5 The definition of aromatic moiety includes phenyl, polyaromatic and fused aromatic moieties. Inertly-substituted means the substituent groups are essentially inert to the cyclopentadienone and acetylene polymerization reactions and do not readily react under the conditions of use of the cured polymer in microelectronic devices with environmental species such as water. Such substituent groups include, for example, F, Cl, Br,  $-CF_3$ ,  $-OCH_3$ ,  $-OCF_3$ ,  $-O-Ph$  and alkyl of from one to eight carbon atoms, cycloalkyl of from three to about eight carbon atoms. For example, the moieties which can be unsubstituted or inertly-substituted aromatic moieties include:
- 10

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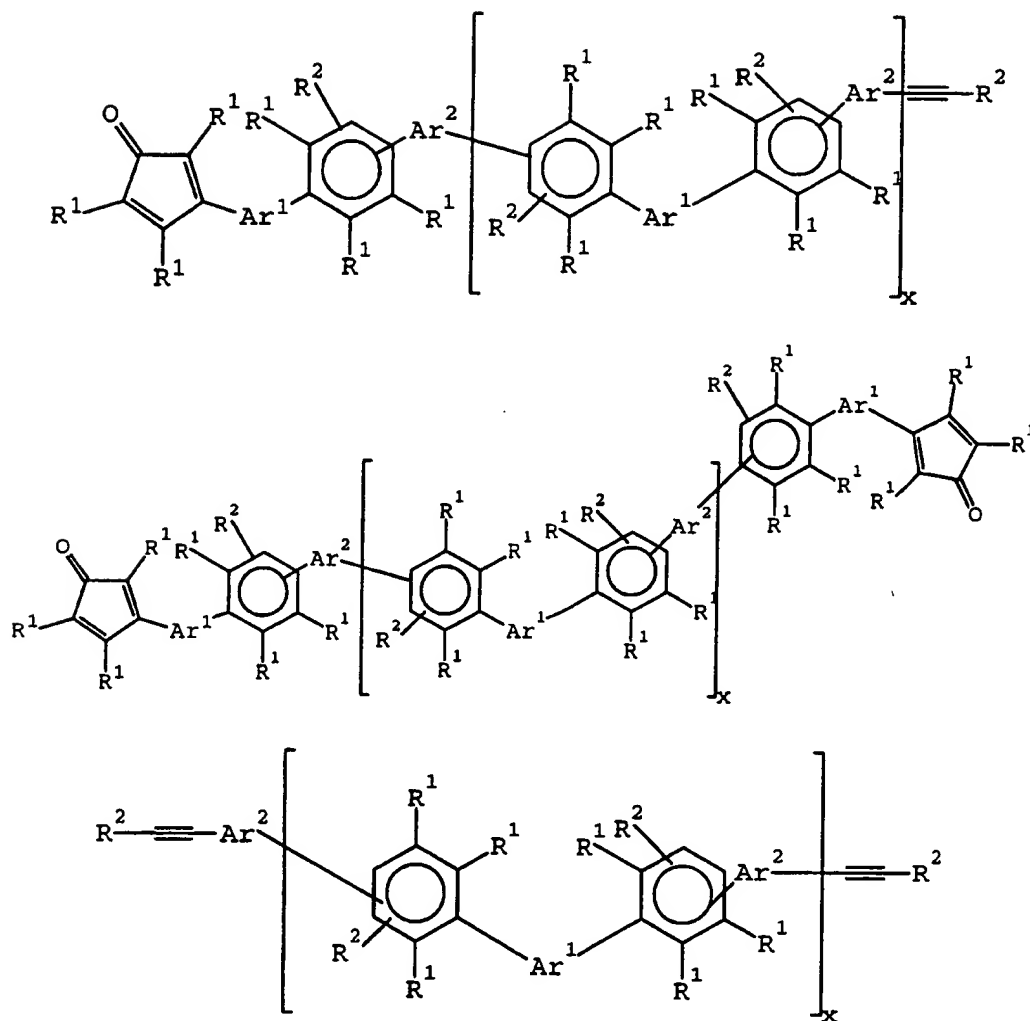


- 5 wherein Z can be: -O-, -S-, alkylene, -CF<sub>2</sub>-, -CH<sub>2</sub>-, -O-CF<sub>2</sub>-, perfluoroalkyl, perfluoroalkoxy,

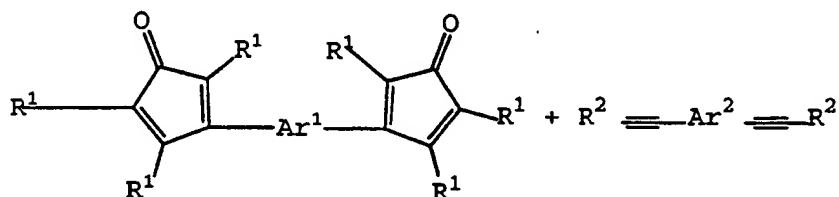


wherein each R<sup>3</sup> is independently -H, -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>,  
-(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> or Ph. Ph is phenyl.

- 10 II. Polyphenylene oligomers and polymers of the general formulas:

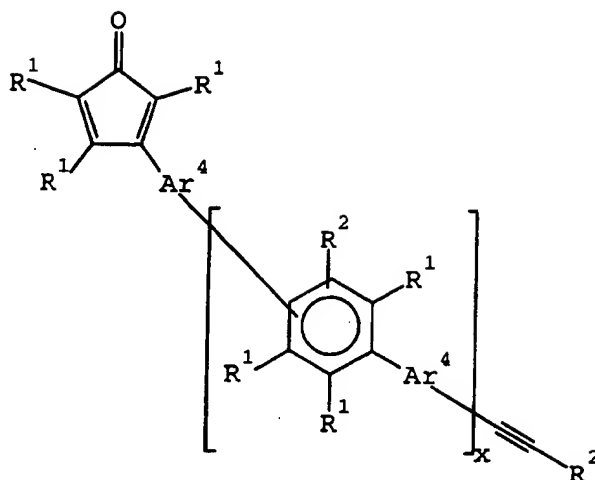


wherein  $R^1$ ,  $R^2$ ,  $Ar^1$  and  $Ar^2$  are as defined previously; and  $x$  is an integer from 1 to about 1000. Preferably,  $x$  is from 1 to about 50 and more preferably from 1 to about 10. Such oligomers and polymers can be prepared by the reaction of a biscyclopentadienone and a diacetylene of the general formulas:

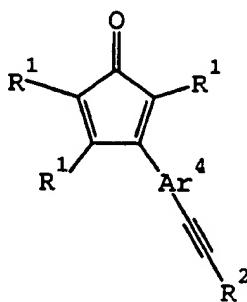


wherein  $R^1$ ,  $R^2$ ,  $Ar^1$  and  $Ar^2$  are as previously defined.

10 III. Polyphenylene oligomers and polymers represented by the formula:

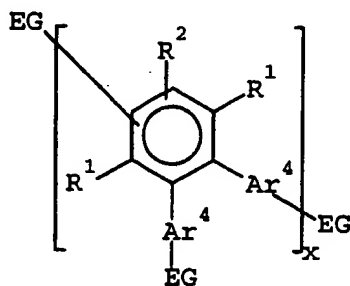


wherein Ar<sup>4</sup> is an aromatic moiety or an inertly-substituted aromatic moiety, R<sup>1</sup>, R<sup>2</sup>, and x are as previously defined, as can be prepared by the reaction of the cyclopentadienone functionality and the acetylene functionality of a polyfunctional compound of the general formula:

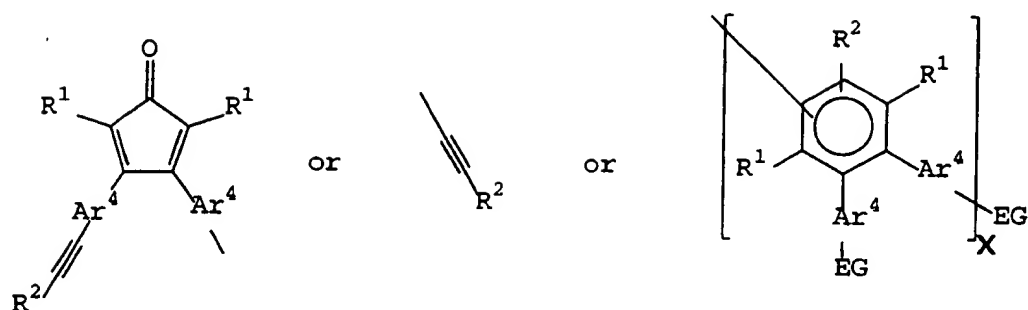


wherein R<sup>1</sup>, R<sup>2</sup> and Ar<sup>4</sup> are as defined previously.

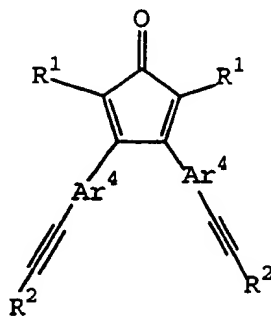
IV. Polyphenylene oligomers and polymers represented by the formula:



wherein EG is represented by any one of the formulas:



wherein  $R^1$ ,  $R^2$ ,  $Ar^4$  and  $x$  are as defined previously, as can be prepared by the reaction of the cyclopentadienone functionality and the acetylene functionality of a polyfunctional compound of the general formula:



5

wherein  $R^1$ ,  $R^2$ , and  $Ar^4$  are as defined previously.

A polyfunctional compound containing two or more aromatic cyclopentadienone moieties may be made by the condensation of benzils with benzyl ketones using conventional methods. Exemplary methods are disclosed in Kumar et al. Macromolecules, 1995, 28, 124-130; Ogliaruso et al., J. Org. Chem., 1965, 30, 3354; Ogliaruso et al., J. Org. Chem., 1963, 28, 2725; and U.S. Patent 4,400,540; all of which are incorporated herein by reference.

A polyfunctional compound containing two or more aromatic acetylene moieties may be made by conventional methods. An aromatic compound may be halogenated and then reacted with the appropriate substituted acetylene in the presence of an aryl ethynylation catalyst to replace the halogen with the substituted acetylene compound.

Once the polyfunctional compound monomers are made, they are preferably purified. In particular, in preparation for use as an organic polymer dielectric, metals and ionic species are removed. For example, the polyfunctional compounds containing aromatic acetylene groups may be contacted with a water wash, an aliphatic hydrocarbon solvent

and then dissolved in an aromatic solvent and filtered through a purified silica gel. This treatment can remove residual ethynylation catalyst. Additional recrystallizations may also help in removal of undesired impurities.

While not intended to be bound by theory, it is believed that the  
5 polyphenylene oligomers and polymers are formed through the Diels Alder reaction of the cyclopentadienone groups with the acetylene groups when the mixtures of cyclopentadienones and acetylenes in solution are heated. These oligomers may contain cyclopentadienone and/or acetylene end groups and/or pendant groups. Upon further heating of the solution or an article coated with the solution, additional chain extension can  
10 occur through the Diels Alder reaction of the remaining cyclopentadienone end groups with the remaining acetylene groups resulting in an increase in molecular weight. Depending on the temperature used, reaction of the acetylene groups with each other may also occur.

The oligomers and polymers are shown in the structures as having either cyclopentadienone and/or acetylene end groups and/or pendant groups. In general, the  
15 end groups will depend on the relative concentration of cyclopentadienone to Diels Alder reactive acetylene functionality employed in the reaction, with a stoichiometric excess of cyclopentadienone functionality giving more cyclopentadienone end groups and a stoichiometric excess of Diels Alder reactive acetylene functionality giving a greater proportion of acetylene end groups.

20 Mixtures or copolymers of two or more different polyarylenes may also be employed. In addition, the composition can contain other monomers copolymerizable with the monomers which form the polyarylene. The polyarylene may be used in the form of a monomer, an oligomer, a polymerized or copolymerized resin, a prepolymer, i.e., a partially polymerized or copolymerized polyarylene having reactive polymerization sites which  
25 provide for further polymerization, or mixtures thereof (i.e., polymer precursors) in forming the crosslinked low dielectric constant polymer of the coating composition.

The coating compositions may also contain other additives to impart other useful properties to the film forming compositions. Such additives include but are not limited to photocrosslinking agents such as bis(arylazides), e.g., 2,6-bis(4azidobenzylidene)-4-  
30 ethylcyclohexanone or 2,2-bis(4-(4-azidophenoxy)-phenyl)propane, energy transfer agents (exemplified in WO 9312055), anti-oxidants (exemplified in U. S. Patent No. 5,185,391) and the like.

The amounts of the silane, solvent, and polymer precursors employed in the coating composition is dependent upon a number of factors including the specific end-use

application and the properties desired. One such application is an adhesion promoter primer coating. As mentioned, a promoter primer coating provides adhesive bonding between the surface to which it is applied and a subsequently applied coating layer. Alternatively, the composition is a self-priming coating. In such a case, the hydrolyzed silane functions to provide adhesive bonding between the surface to which the self priming formulation is applied and the resultant film. In addition, it can also provide adhesive bonding to a subsequently applied surface. In general, a primer composition normally will contain lesser amounts of the cross linking prepolymer, oligomer, resin or mixtures thereof than when the composition is used as a self-priming composition.

In general, regardless of its intended end-use, the composition comprises from about 0.01 to about 10 weight percent hydrolyzed silane, from about 10 to about 99.9 weight percent solvent, and from about 0.01 to about 90 weight percent cross linking prepolymer, oligomer, resin or mixtures thereof, said weight percents being based on the total weight of the composition.

In general, when applied as an adhesion promoter primer coating application, the composition comprises from about 0.01, more preferably from about 0.2, most preferably from about 0.3 weight percent, to about 10, more preferably about 5, and most preferably to about 2.5 weight percent of the hydrolyzed silane; from about 75, more preferably about 90, and most preferably about 92.5 weight percent to about 99.9, more preferably about 99.5, and most preferably about 98 weight percent of solvent, and from about 0.01, more preferably from about 1, and most preferably from about 2 weight percent to about 20, more preferably about 10, and most preferably about 5 weight percent of polymer precursors, said weight percents being based on the total weight of the composition.

Alternatively, when employed as a self-priming coating application, the composition comprises from about 0.01, more preferably from about 0.2, and most preferably from about 0.5 weight percent to about 5, more preferably to about 3, and most preferably to about 1 weight percent of hydrolyzed silane; from about 10, more preferably from about 20, and most preferably from about 35 weight percent to about 95, more preferably to about 90 and most preferably to about 80 weight percent of solvent; and from about 5, more preferably from about 10, and most preferably from about 20 weight percent to about 90, more preferably to about 80, and most preferably to about 65 weight percent of cross linking prepolymer, oligomer, resin or mixtures thereof, said weight percents being based on the total weight of the composition.

While the coating compositions can be applied using any of the techniques well known in the art, such as spray, brush, dip, meniscus, extrusion, capillary, curtain, roll



coating and the like, they are advantageously applied at room temperature using conventional spin-coating techniques.

5 In this application, the coating composition can be used as an adhesion promoter primer layer or as a self-priming polymer layer. Typical thicknesses for adhesion promoter primer layers are between about 30 to about 1000 Angstroms, whereas the thickness of the self-priming polymer layer can vary from about 0.1 to about 25 microns. Multiple layers may be prepared using the composition either as an adhesion promoter primer or a self-priming polymer layer. The multi-layer coatings typically range between about 10 to about 500 microns and are preferably from about 50 to about 200 microns. The coating compositions  
10 of the present invention may also be subsequently coated with other polymeric materials such as arylcyclobutene or polyphenylene polymers and copolymers or any other polymeric material which will bond with the coating composition.

After being applied, the coating compositions can be crosslinked, photocrosslinked, cured or soft cured. Photodefineable low dielectric constant polymers are typically  
15 photocrosslinked prior to further cure. Conventional curing techniques such as electron beam, ultra violet, thermal radiation, or convection can also be employed.

The degree of polymerization will depend upon the application involved. For instance, when additional layers will be applied, a soft cure or crosslinking of about 80 to 85 percent (as measured, for example, by FTIR) is preferred and can be accomplished, for  
20 example, by heating at about 220°C for about 30 minutes. In the final stage of curing, crosslinking of more than about 95 percent can be achieved, for example, by heating at 250°C for about 1 hour.

The hydrolyzed or partially hydrolyzed silanes used in the coating composition of the present invention may be prepared according to the method disclosed in WO96/11990,  
25 preferably by a solventless approach where the silane is contacted with a sufficient amount of water to hydrolyze at least one alkoxy or acyloxy group. Acid or base catalysts may optionally be employed.

In coating articles for use in electronics applications such as multichip modules, flat panel displays, integrated circuits, and the like, it has been surprisingly discovered that a  
30 coating comprising the crosslinked low dielectric constant polymer of a crosslinking prepolymer, oligomer, resin or mixture thereof and a hydrolyzed or partially hydrolyzed alkoxysilane may be adhered to a surface of a substrate comprised of a first material that is a metal, ceramic or polymer and a second material that is (i) a metal, ceramic or polymer and (ii) different than the first material.

Exemplary metals include aluminum, copper, tungsten, gold, platinum, silver, titanium and chrome. Exemplary ceramics include alumina, silica, MgO, BeO, including spinels, aluminum nitride, boron nitride, silicon nitride, titanium nitride, gallium arsenide; and glasses such as fiber glass, lime glass, flint glass, borosilicate glass, PYREX® and  
5 VYCOR®. Exemplary polymers include those described herein and polyimides, epoxies and polyamides.

In particular and surprisingly, the coating is adhered to a surface, of a substrate, comprised of silicon or thermally oxidized silicon (i.e., first material) and a metal such as aluminum or copper (i.e., second material). The substrate surface may even be comprised  
10 of other materials including, for example, aluminum nitride, silicon nitride, silicon oxynitride, titanium nitride, tungsten and other materials used to fabricate microelectronic devices. The substrate surface may even be comprised of silicon, copper and aluminum.

The following examples are set forth to illustrate the present invention and should not be construed to limit its scope. In the examples, all parts and percentages are by  
15 weight unless otherwise indicated.

#### Example 1

In preparation of the spin coating composition and substrate of this Example, the following two monomers and then polyphenylene resin solution were made as follows.

The first monomer 1,3,5-Tris(phenylethynyl)benzene was made as follows.  
20 Triethylamine (375 g), triphenyl phosphine (4.7865 g), palladium acetate (1.0205 g), and N,N-dimethyl formamide (2000 mL) were charged to a 5 liter 3-necked round bottom flask equipped with a thermocouple, an overhead mechanical stirrer, a condenser, an addition funnel, and a heating mantle with a temperature controller. This mixture was stirred for 5 minutes to dissolve the catalyst. Then diethylhydroxylamine (5 g), 1,3,5-tribromobenzene  
25 (190 g) and phenylacetylene (67.67 g) were added. The reactor was purged with nitrogen for 15 minutes, and then heated to 70°C while maintaining a nitrogen atmosphere. After heating at 70°C for 30 minutes, phenylacetylene (135.33 g) was slowly added dropwise over a period of about 1 hour, and the temperature increased to 80°C. Heating was continued an additional nine hours. The reaction was then cooled to room temperature and  
30 water (1 liter) was added which precipitated crude product. The product was filtered, washed three times with 500 mL portions of water, then once with 500 mL of cyclohexane. The crystals were vacuum dried at 75°C overnight to give 226.40 g (99.1% yield) that is 97.25 area % pure by gas chromatography. The crystals were dissolved in toluene (1800

mL), refiltered through silica gel, and the solvent removed on a rotary evaporator to give 214.2 g (94.2% yield) that was 99.19 area % pure by gas chromatography. The residue was then recrystallized from a mixture of toluene (375 mL) and 2-propanol (696 mL). The white crystals were filtered, rinsed with a mixture of toluene (100 mL) and 2-propanol (400 mL), and vacuum dried at 75°C overnight to give 1,3,5-tris(phenylethynyl)benzene (190.0 g, 83.91% yield) that is 99.83 area % pure by gas chromatography. Additional recrystallizations from toluene/isopropanol gives material of acceptable organic and ionic purity.

The second monomer 3,3'-(Oxydi-1,4'-phenylene)bis(2,4,5 triphenylcyclopentadienone) herein DPO-CPD was made as follows.

First 4,4'-diphenylacetyldiphenyl ether was prepared as follows. To a slurry of aluminum chloride (97.9 g, 0.734 mol) in methylene dichloride (200 mL) at 0°C was added, dropwise, a solution of diphenyl ether (50.0 g, 0.294 mol) and phenylacetyl chloride (102 g, 0.661 mol) in methylene chloride (50 mL), over a 30 minute period. When the addition was completed, the reaction mixture was allowed to warm to ambient temperature and stirred overnight. The reaction mixture was carefully poured, with stirring, into 1.5 kg of ice/water. Methylene chloride (1500 mL) was added to dissolve the solids and the layers were separated. The organic layer was filtered through celite, then concentrated to dryness. Recrystallization from toluene gave 110 g (92 percent) of the ether as light tan prisms.

Second 4,4'-Bis(phenylglyoxaloyl)diphenyl Ether was prepared as follows. Aqueous HBr (97 mL of a 48 weight percent solution) was added to a slurry of 4,4'-diphenylacetyldiphenyl ether (50.0 g, 0.123 mol) in DMSO (400 mL) and the resulting mixture was heated to 100°C for two hours, then cooled to ambient temperature. The reaction mixture was partitioned between toluene (500 mL) and water (750 mL). The organic layer was washed with water (3 X 250 mL), followed by washing with brine, and concentration to give a viscous, bright yellow oil which solidified upon standing at ambient temperature. Recrystallization from ethanol gave 35.9 g (67 percent) of this ether as bright yellow cubes.

Then, to a nitrogen purged 5-L Morton flask equipped with a thermocouple, reflux condenser with nitrogen inlet, mechanical stirrer, and addition funnel was added, 195.4 g (0.4498 mol, 1.0 eq) 4,4'-bis(phenylglyoxaloyl)diphenyl ether, 193.9 g diphenylacetone (0.9220 mol, 2.05 eq), and 2.5 L deoxygenated ethanol. The mixture was heated to reflux, at which point a homogeneous solution was attained, and the solution was sparged with nitrogen for 30 minutes. To the addition funnel was added a solution containing 25.2 g

KOH (0.4498 mol, 1.0 eq), 200 mL ethanol, and 25 mL water. The temperature was reduced to 74°C and the KOH solution was added rapidly over 5 minutes. An exothermic reaction was quickly established and maintains reflux until three quarters of the solution was added whereafter the temperature begins to decrease. A dark purple color was observed immediately upon addition of base and solid was observed before addition was complete. After complete addition, the heterogeneous solution was heated at strong reflux for 15 minutes and much solid product was formed. The mixture was allowed to cool to 25°C and 29.7 g glacial acetic acid (0.4948 mol, 1.1 eq.) was added and stirred for 30 minutes. The crude product was isolated by filtration and washed in the filter funnel with, 1 L water, 3 L EtOH, 2 L MeOH, and dried for 12 hours at 60°C to 90°C under vacuum giving 323 g (92%) crude DPO-CPD which was 94% pure by LC. The crude material was dissolved in HPLC grade methylene chloride (10 wt%), transferred to a 5-L Morton flask equipped with a bottom flush valve and mechanical stirrer, and washed vigorously for 10 to 90 minutes, 2 to 7 times with equal volume portions of low ionic water. The CH<sub>2</sub>Cl<sub>2</sub> solution was then flashed through a 5 cm column containing 75 g of silica gel in CH<sub>2</sub>Cl<sub>2</sub>. The column was washed with an additional 1 L CH<sub>2</sub>Cl<sub>2</sub> at which point the filtrate was essentially clear. The solution was evaporated to dryness and re-dissolved in THF and evaporated again to remove the bulk of the residual methylene chloride. The powder was transferred to a 5 L flask equipped with addition funnel and Friedrichs reflux condenser, and dissolved (0.07-0.12 g/mL) in deoxygenated HPLC THF at reflux. An additional 1 L THF was then added and a nitrogen sparge tube was inserted into the solution. The solution was sparged with nitrogen for three hours and the THF was condensed at 45°C to 50°C while residual methylene chloride was removed by distillation. A distillation head was attached and 700 mL to 1 L THF was removed. The solution was then allowed to slowly cool over several hours to room temperature then cooled with an ice bath to below 10°C during which time crystallization occurs. The crystals were isolated using a 5 mm PTFE filter in a 4-L Millipore clamp-frit suction filtration flask. The crystals were then washed with 1-L MeOH and dried over night at 80°C to 90°C under vacuum giving 70 to 85% yield DPO-CPD with 99% LC purity, mp 270°C.

The 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) (100.0 g, 0.128 moles), low ionic 1,3,5-tris(phenylethynyl)benzene (48.3 g, 0.128 moles), and electronic gamma butyrolactone (346 g) were added to a Pyrex® 1-L 3-necked round bottom flask which had been rinsed with deionized water and HPLC grade acetone and dried. The flask was attached to a nitrogen/vacuum inlet. The magnetically stirred solution was degassed by applying vacuum and refilling with nitrogen five times. Nitrogen gas was

then allowed to flow through the headspace of the flask and exit through a mineral oil bubbler. The solution was then heated to an internal temperature of 200°C. After about 48 hours of heating the solution was allowed to cool and was transferred into a bottle made of tetrafluorethylene. Analysis of the final solution by gel permeation chromatography indicated a  $M_n=8250$  and a  $M_w=29000$  relative to a polystyrene standard. Analysis of the final solution by reverse phase chromatography indicated a residual 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) level of 1.8 weight percent. This solution was mixed with an amount of cyclohexanone to make the polyphenylene resin solution have a viscosity of about 17 centistote.

10 Vinyltriacetoxysilane(VTAS), available from Dow Corning Corp., Freeland MI, under the product number Z-6075 was mixed with deionized water having a resistivity of 18M $\Omega$  in a ratio of 3 moles water/mole of VTAS. This mixture was stirred with a magnetic stirring bar for about 45 minutes. 0.62 parts by weight (pbw) of this hydrolyzed VTAS solution was mixed with 99.38 pbw of the polyphenylene resin solution.

15 An amount of the coating mixture sufficient to form a 1.5 micrometer thick coating was syringe-dispensed through a 0.1 micron filter onto a thermally-oxidized silicon wafer. Coating was carried out using an MTI spin coater and hot-plate modular track system (Machine Technology, Inc. Parsippany, NJ). The coating was performed in the following steps: (i) the coating mixture was dispensed within 10 seconds while the wafer was rotated at 50 rpm; (ii) the wafer was rotated at 250 rpm for 3 seconds to spread the coating mixture over the wafer; (iii) the wafer was spun for 20 seconds at approximately 1500 rpm; and (iv) a backside rinse of the wafer was carried out during the spin cycle to remove the perimeter edge-bead. The back-side rinse solvent was mesitylene. Rinsing began at start of the 1500 rpm spin-cycle and continued for 6 seconds, and then ceased for the last 14 seconds to permit drying of the mesitylene solvent.

After coating, the wafer was transferred under automated control to the hot-plate module (iv) for 5 seconds of proximity-bake at a height of 0.25 centimeters and a temperature of 320°C with a concurrent nitrogen purge of the head-space, followed by (v) a vacuum-contact bake of the wafer at 320°C for 90 seconds under continuous nitrogen purge, followed finally by a nitrogen proximity-bake at a height of 2.25 centimeters and a temperature of 320°C for 10 seconds to produce a gradual cool-down. The substrate and coating were then soft-cured in a Yield Engineering Systems (YES) oven under a continuous nitrogen purge. Nominal steps in the soft-curing program were: (i) to ramp in 2.5 hours from the ambient temperature to 400°C, then (ii) to hold 400°C for 6 minutes, then (iii) to cool to a temperature below 200°C before removing parts from the oven.

The dispensing, coating, hot-plate baking and soft curing were repeated to make a soft cured polyphenylene coating that was about 3 micrometers thick. Finally, a third layer was dispensed, spin-coated and hot-plate baked to form an about 5 micrometer thick coating which was then hard-cured (cross-linked) using the following steps in the oven program under continuous nitrogen purge: (i) ramp in 2.5 hours from the ambient temperature to 400°C; then (ii) hold 400°C for 20 minutes; then (iii) ramp in 30 minutes to 450°C; then (iv) hold 450°C for 6 minutes; then (v) cool to a temperature below 200°C before removing parts from the oven.

The above procedure was repeated for (1) a thermally oxidized silicon wafer sputter coated with aluminum (sputter target was aluminum containing 1% by weight copper), (2) a thermally oxidized silicon wafer coated with silicon-nitride by plasma enhanced chemical vapor deposition and (3) a thermally oxidized silicon wafer coated with titanium-nitride by plasma enhanced chemical vapor deposition. For each of these coated substrates, values of bond strength were obtained from the level of delamination observed by optical microscopy subsequent to microindentation described previously. The results for each substrate are shown in Table XI.

TABLE XI

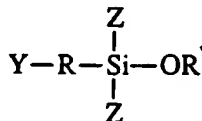
Hydrolyzed VTAS Concentration (wt%)	Film Thickness ( $\mu\text{m}$ )	ADHESION BOND STRENGTH TO			
		Si (MPa)	Al (MPa)	$\text{Si}_x\text{N}_y$ (MPa)	TiN (MPa)
0*	5.2	55	37	69	217
0*	5.2	38	41	73	216
0.5	5.2	124	107	150	233
0.5	5.2	122	111	152	243

\* Comparative Example (were made the same way as Example 1 but without any hydrolyzed VTAS)

From Table XI it is readily apparent that a substrate of the present invention may be made having a uniformly coated and well adhered coating of the crosslinked low dielectric polymer even when the substrate has two or more different materials at its surface. Whereas, in the absence of the alkoxysilane, the coated substrate of this invention is not made.

## CLAIMS:

1. A composition comprising:
  - a) a hydrolyzed or partially hydrolyzed silane selected from  
5 alkoxy silanes and acyloxy silanes,
  - b) a solvent consisting of an organic liquid or mixture of two or more organic liquids in which component (a) and component (c) are soluble and
  - c) a crosslinking prepolymer, oligomer, resin or mixtures thereof that forms a low dielectric constant crosslinked polyarylene.
- 10 2. The composition of Claim 1 wherein the silane has been hydrolyzed with from about 10 percent of a stoichiometric amount to an amount of water required for complete hydrolysis.
3. The composition of Claim 1 wherein the silane has been hydrolyzed by water present in: the solvent; the crosslinking prepolymer, oligomer, resin or mixtures thereof; or  
15 mixtures thereof.
4. The composition of any one of Claims 1-3 wherein the silane is of the formula:



- 20 wherein R is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Y is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethylamino, or 3-amino; R' is independently in each occurrence C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>1</sub>-C<sub>6</sub> acyl; and Z is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl or OR'.
- 25 5. The composition of any one of Claims 1-3 wherein the silane is vinyl triacetoxysilane.
6. The composition of any one of Claims 1-3 wherein the solvent is mesitylene, cyclohexanone, gammabutyrolactone, N-methylpyrrolidinone, or mixtures thereof.
7. The composition of any one of Claims 1-3 wherein the polyphenylene is of  
30 monomers comprising 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) and

1,3,5-tris(phenylethynyl)benzene.

8. The composition of Claim 1 wherein:

the hydrolyzed or partially hydrolyzed silane is from about 0.01 to about 10 weight percent,

5 the solvent is from about 10 to about 99.9 weight percent, and

the crosslinking prepolymer, oligomer, resin or mixtures thereof that forms a low dielectric constant crosslinked polyarylene is about 0.01 to about 90 weight percent,

said weight percents being based on the total weight of the composition.

9. An article comprising:

10 (a) a substrate that has a surface having a region of a first material comprising a metal, ceramic or polymer and a region of a second material comprising (i) a metal, ceramic, or polymer and (ii) different than the first material and

(b) a coating adhered to the surface of the substrate, the coating being comprised of a crosslinked low dielectric constant polyarylene and a hydrolyzed or partially hydrolyzed  
15 silane selected from alkoxysilanes and acyloxysilanes.

10. The article of Claim 9 wherein the first material is silicon or thermally oxidized silicon and the second material is aluminum or copper.

11. The article of Claim 10 wherein the crosslinked polymer is of the polyphenylene prepolymer, oligomer, resin or mixtures thereof, the polyphenylene  
20 prepolymer, oligomer, resin or mixtures thereof being of monomers comprising 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) and 1,3,5-tris(phenylethynyl)benzene.

12. The article of Claim 10 or 11 wherein the silane is vinyltriacetoxysilane.



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/19242

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C09D165/02 C09D171/12

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09D C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 11149 A (DOW CHEMICAL CO) 19 March 1998 (1998-03-19) cited in the application claims 1-27 page 15, line 12 - line 14 page 17, line 3 - line 11 page 18, line 17 - line 31 ---	1
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 467 (C-550), 7 December 1988 (1988-12-07) & JP 63 186762 A (TORAY SILICONE CO LTD), 2 August 1988 (1988-08-02) abstract ---	1
X	EP 0 771 830 A (CIBA GEIGY AG) 7 May 1997 (1997-05-07) claim 1 ---	1
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

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- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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- "&" document member of the same patent family

Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/19242

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 182 163 A (GEN ELECTRIC) 28 May 1986 (1986-05-28) claim 1 ---	1
A	EP 0 457 351 A (MITSUBISHI PETROCHEMICAL CO) 21 November 1991 (1991-11-21) claims 1-11 ---	1
P,A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 1999-502462 XP002126332 & JP 11 217490 A (NIPPON GOSEI GOMU KK), 10 August 1999 (1999-08-10) abstract -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/19242

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9811149 A	19-03-1998	US 5965679 A EP 0889920 A NO 985617 A	12-10-1999 13-01-1999 01-12-1999
JP 63186762 A	02-08-1988	JP 2030872 C JP 7049516 B	19-03-1996 31-05-1995
EP 0771830 A	07-05-1997	CA 2189311 A JP 9183833 A	03-05-1997 15-07-1997
EP 0182163 A	28-05-1986	JP 1678085 C JP 3043307 B JP 61120855 A US 5061746 A	13-07-1992 02-07-1991 07-06-1986 29-10-1991
EP 0457351 A	21-11-1991	JP 4023831 A JP 4033923 A JP 4077552 A JP 4077553 A JP 4126742 A US 5177156 A	28-01-1992 05-02-1992 11-03-1992 11-03-1992 27-04-1992 05-01-1993
JP 11217490 A	10-08-1999	NONE	